# Synthesis and characterization compounds of Vanadium (IV)

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# Síntesis y caracterización de compuestos de Vanadio (IV)

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# Síntese e caracterización de compostos de Vanadio (IV)

**Diploma**

**Uniwesytet Gdański and Universidade da Coruña**

**Bachelor degree in chemistry**

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# 1. INTRODUCTION

The compounds under study, vanadium(IV) complexes, have different ligands, which differ both in structure and function from each other.

Due to the high ionic potential (the ratio of the formal ion charge to the radius), simple $V^{4+}$ cations are not found in aqueous solutions. Vanadium on the +4 oxidation state is present in the form of oxocation, i.e. $[VO(H_2O)_5]^{2+}$ (vanadyl cation, $VO^{2+}$), which can be obtained by dissolving $VOSO_4$ salt (Fig. 1) in the acidic environment [1].
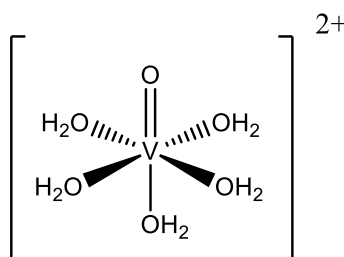


**Figure1. The structure of [VO(H2O)5]2+ 1**

The $[VO(H_2O)_5]^{2+}$ ions do not undergo atmospheric oxygen at low pH, while at neutral and basic pH they oxidize to orthovanadium ions, $VO_4^{3-}$. Also, ligand-bound vanadyl ions can be oxidized. Examples are VO2+ complexes with albumin and transferrin, whose half-oxidation times are 6.5 and 8.1 min respectively. [2]. Vanadyl aquacomplexes are also sensitive to pH changes [3]. In the physiological pH range, vanadyl ions are easily hydrolysed, resulting in hydroxycomplexes and multi-core complexes, for example: $[VO(OH)]^+$(logβ = -5,94), $[(VO)_2(OH)_2]^{2+}$(logβ = - 6.95), $[VO(OH)_3]^-$ (logβ = -18.0) and $[(VO)_2(OH)_5]^-$(logβ = -22.5 [4]. Due to the high affinity of vanadyl ions to ligands, which have oxygen, nitrogen, phosphorus or sulfur donor atoms, in biological tests carried out in buffer solutions, an additional, so-called competitive equilibrium reaction between the buffer solution components and the $VO^{2+}$ ion. The most frequently used buffer for testing the chemical activity of vanadyl ions is the HEPES buffer (*N*-(2-hydroxyethyl)piperazine-*N*-ethanesulfonic acid), due to its poor complexing properties.

The ligands used in the different syntheses determine the differences in structure and behavior of the different oxovanadium compounds. The ligands used are:

Aquo ligand: it is a ligand with neutral charge, monodentate and sigma donor, which is linked to the central metal by oxygen.

Oxydiacetate (Oda): it is neutral loads tridentate ligand which can be coordinated with different electron-acceptor ions to form chelated rings.

Bipyridine (bpy): it is a ligand with neutral charge, bidentate and sigma donor, linked to the central metal by two different nitrogens.

Phenantroline (Phen): this one is the same case than above, bipy, neutral charge, bidentate and sigma donor.

Phenantroline is linked to the central atom strongerthan bipyridine, because the nitrogens donors chelating are previously organized. Nevertheless, phenantroline is a weaker donor than bipyridine.

The ligands water, bpy and phen can be found in the spectrochemical series (crystal field theory), while water appears in the middle of the series; the ligands bypi and phen appear to the right of it. This implies that the nitrogenous ligands of the experiment are "weak field" ligands. Water can behave both as a "strong field" ligand and as a "weak field" ligand, since it will depend on the type of metal to which it is attached, the oxidation state of the metal and the synthesis conditions.

This is important because it explains many of the properties observed in substances; in this case, it can account for the transitions between orbitals. This also can help us to understand, for example, the colour of the compounds. The wavelength of the absorption is determined by the magnitude of the split between the substances energies of the orbitals d of the surrounding ligands.

The greater the unfolding, the shorter the wavelength of the absorption corresponding to the transition of the electron from the orbital of low energy to the highest energy.

## 1.1. The crystal structure description of $VO(oda)(H_2O)_2$

The $VO(oda)(H_2O)_2$ complex has vanadium as its central metal, which acts with an oxidation state of 4. This compound is formed by a vanadyl group and carboxylate and water groups acting as ligands. It contains a set of donor OOO ligands. However, initial calculations reveal that the mer↔fac energetic barrier is small enough and thus the co-existence of both isomers in the solution at the equilibrium is possible [5]. It is a blue

crystalline solid that is stable to oxidation in contact with air. The complex solutions have an acidic nature.

The crystalline structure of the complex has C2v symmetry (Fig. 2). The coordination geometry around the vanadium is a distorted octahedron. This distortion is due to the union of the trident oda ligand.
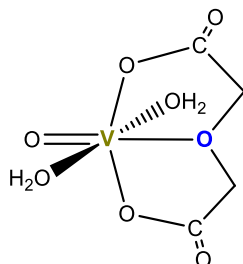


Figure 2. The structure of [VO(oda)(H2O)2]

The aqueous ligand is in a *trans* position with respect to the central atom, while the oxidiacetate ligand is distributed in a southern manner.

The scheme of thesynthesis reaction that takes place to obtain the VO(oda)(H$_2$O)$_2$ is presented in Figure 3.
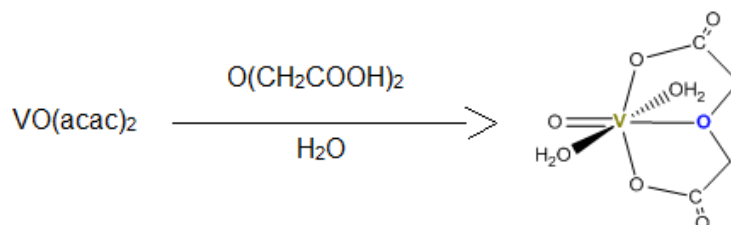


Figure 3. The scheme of the synthesis of [VO(oda)(H2O)2]

The molecular structure has been determined by X-ray diffraction methods. The first column of the following table reports selected bond lengths of the present structure. Each complex molecule posses an inner two-fold axis coinciding with the vanadyl group and the central oxygen atom of oda. The water ligands are mutually trans while the oxydiacetate ligand is southernly distributed. A similar mer disposition metal complex. Ideal octahedral geometry cannot be achieved as the adjacent bites of the tridentate oda ligand are only 73.05⁰. Selected geometric parameters for VO(oda)(H$_2$O)$_2$ are collected in Table 1.
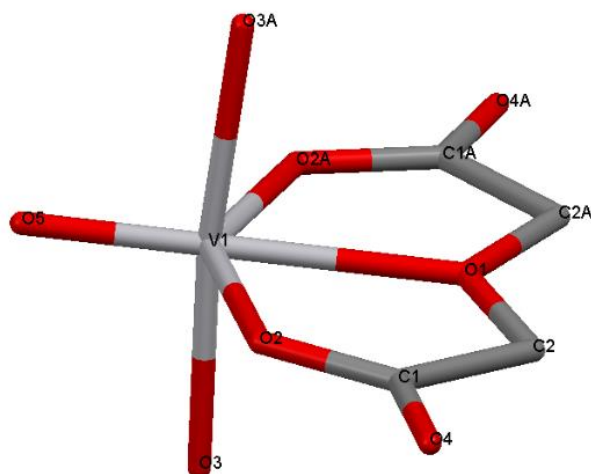
**Figure 4.** Molecular structure of [VO(oda)(H2O)2]. Simulated structure by Mercury 3.10 program

**Table 1.** Selected geometric parameters of [VO(oda(H2O)2]. [6]

| BOND | DISTANCE (Å) |
|---|---|
| V(1) – O(1) | 2.176 |
| V(1) – O(2) | 2.017 |
| V(1) – O(2A) | 2.017 |
| V(1) – O(3) | 2.042 |
| V(1) –O(3A) | 2.042 |
| V(1) – O(5) | 1.586 |

## 1.2.     The crystal structure description of [VO(oda)(phen)]·1.5H$_2$O

The [VO(oda)(phen)]·1.5H$_2$O complex has vanadium as its central metal, which acts with an oxidation state of 4. This compound is formed by a vanadyl group and carboxylate and water groups acting as ligands (Fig. 5). It contains a set of donor OOO ligands, but here it is found the influence of another ligand as it is the phenantroline that it is a sigma donor ligand where the two nitrogens donate their electronic pair to the transition metal.

It is a semi-compact crystalline solid of green color. This complex may be dissolved in water although it has low solubility in it, but it is not soluble in solvents of low polarity. It is stable air, both in solution and in the solid state.

The vanadium metal has a distorted octahedral environment and the overall geometry of the compound. The oxydiacetate adopts the fac disposition and the central oxygen atom lies trans to the oxido group.
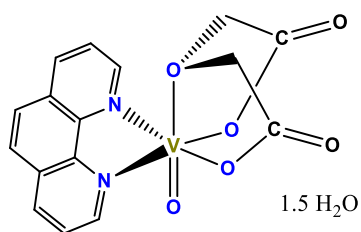


**Figure 5.** The structure [VO(oda)(phen)]·1.5H2O

In the [VO(oda)(phen)]·1.5H$_2$O complex the crystallization water molecules are engaged in a hydrogen bonding network. The water molecules present in the complex compound are interconnected to the oda ligand through hydrogen bonds of different distances. These molecules are inside channels that are parallel to the c axis. Its system has a symmetry lower than C$_4$v.

In Figure 6 I have shown the scheme of the synthesis reaction of [VO(oda)(phen)]·1.5H$_2$O.
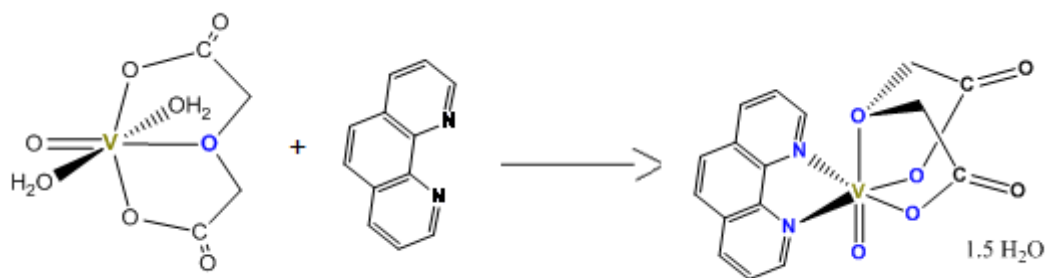


**Figure 6**. The scheme of the synthesis of [VO(oda)(phen)]·1.5H2O

The X-ray study of complex was performed, but the quality of the crystals and of the structural refinement was poor to be presented in detail (Fig. 7). Selected geometric parameters for VO(oda)(H$_2$O)$_2$ are gathered in Table 2.
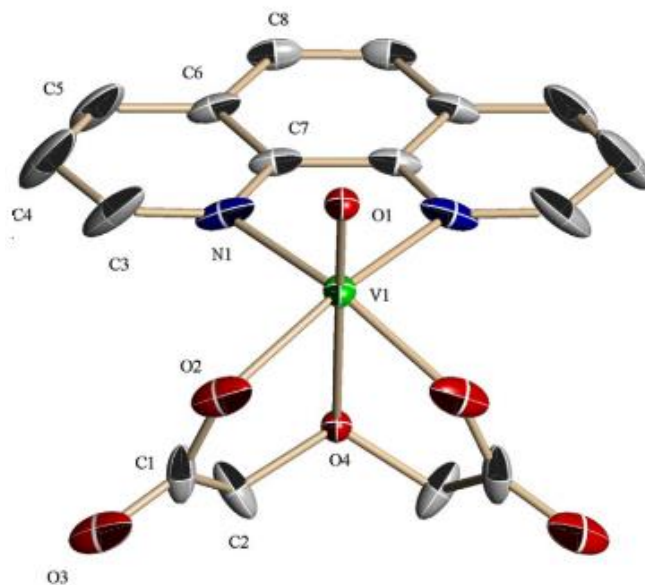
**Figure 7.** Molecular structure of [VO(oda)(phen)]·1.5H2O [1]

**Table 2.** Selected geometric parameters for [VO(oda)(phen)]·1.5H2O [7]

| BOND | DISTANCE (Å) |
|---|---|
| V(1)-O(1) | 1.585 |
| V(1)-O(2) | 1.974 |
| V(1)-N(1) | 2.109 |
| V(1)-O(4) | 2.297 |

As it is possible to observe, the vanadium metal has a distorted octahedral environment and the overall geometry of the compound. The oxydiacetate adopts the fac disposition and the central oxygen atom lies trans to the oxido groups. Selected bond distances and angles of complex are collected in the above table. The V-O(4) (2.297Å) bond distance is longer than the analogous distance in complex [VO(oda)(H$_2$O)$_2$] (2.176Å), where the oda ligand is planar, but is in good agreement with the comparable bond in complex [VO(oda)(bipy)] (2.316Å and 2.334Å) that are trans to a vanadyl group.

In this complex the crystallization water molecules are engaged in a hydrogen bonding network. The water molecules present in the complex compound are interconnected to the oda ligand (O2 and O3) through hydrogen bonds of different distances.

## 1.3.     The crystal structure description of [VO(oda)(bpy)]·H₂O

The [VO(oda)(bpy)]·H$_2$O complex has vanadium as its central metal, which acts with an oxidation state of 4. This compound is formed by a vanadyl group and carboxylate and water groups acting as ligands (Figure 8).

The vanadium metal has a distorted octahedral environment. The ligand oda adopts the fac disposition and, similarly to above compound, the central oxygen atom lies trans to the oxo group.

The overall disposition of the ligands in [VO(oda)(bpy)]·H$_2$O the bipy nitrogen atoms are cis to the oxo ligand. This is not attributed to the different donor capabilities between bipy and phen but likely to the difficult adaptability of dipic to the fac disposition, as it is observed in the Figure 8.
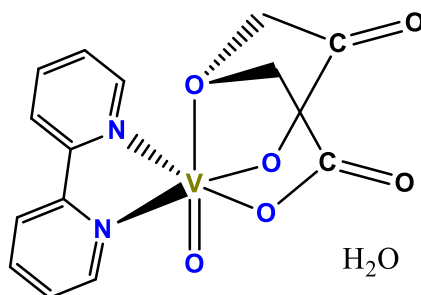


**Figure 8.** The structure of [VO(oda)(bpy)]·H2O

Essentially , in this complex there are no structural differences between the ligands that make up the compound [V(O)(oda)(bipy)].

The quality of the crystals and of the structural refinement is too poor to be presented in detail.

It is a compact crystalline solid with an ochre color. Complexes VO(oda)(bpy)  may be dissolved in water but it is not soluble in solvents of low polarity. It is stable air in solution and in the solid state.

The X-ray structure of compound [V(O)(oda)(bipy)] has been determined. From where the bond lengths between the central atom and the donor atoms of the ligands are obtained. These data are found in the table [reference]

**Table 3**. Selected geometric parameters f or [VO(oda)(bpy)]·H2O [8]

| BOND | DISTANCE (Å) |
|---|---|
| V(1) - O(1) | 1.973 |
| V(1) - O(3) | 2.316 |
| V(1) – O(4) | 1.976 |
| V(1) – N(1) | 2.117 |
| V(1) – N(2) | 2.092 |
| V(1) – O(6) | 1.580 |
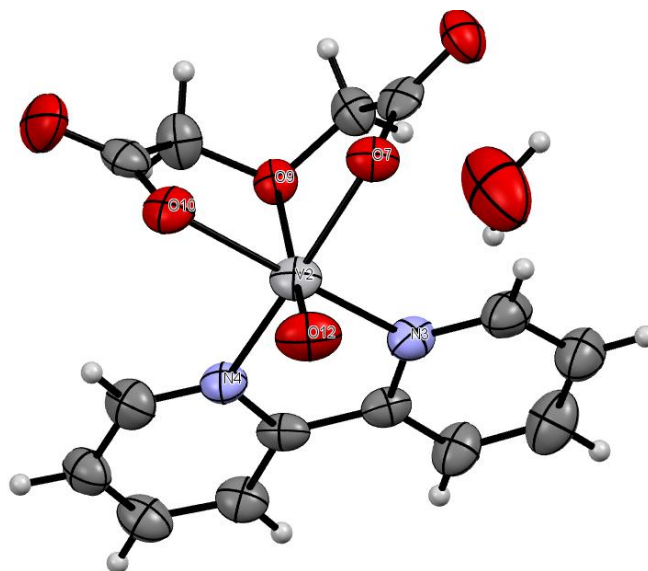


**Figure 9.** Molecular structure of [VO(oda)(bpy)]·H2O [9]

## 1.4.     Biological Properties of Oxovanadium(IV) Complexes

Vanadium is a widespread element in the environment and it is present at trace concentration in biological systems.

When talking about vanadium (IV), it should be taken into consideration that vanadium is unstable at somatic pH and it is also affected by the presence of oxygen. The stability of vanadium compounds in oxidation state +4 is due, among other factors, to the ligands that are coordinated.

Vanadium compounds induce the generation of reactive oxygen species which play an important role in its adverse biological effects, promote apoptosis and convey the cells to death through the increasing of reactive oxygen species levels and disturbance of the redox status, especially by alteration of mitochondria functions in the cells.

Studies with oxovanadium (IV) complexes have demonstrated that some compounds cause substantial single breaks in DNA and produce lipid peroxidation.

Some of the biological properties to be taken into account that vanadium compounds possess are:

*Enzyme inhibition* where the vanadium compounds display insulin mimetic properties such as mitogenic effects, stimulatory and inhibitory action on cell differentiation and numerous metabolic effects.

*Enzyme activation* Vanadium stimulates enzyme activity with the formation of complexes that are similar to the physiological structure due to the binding of vanadium to ligands.

Vanadium compounds also can exhibit antitumor effects as well as toxic and transforming actions in different cell lines; well-known for their antidiabetic effects both on glucose and lipid metabolism, but the mechanisms are still not completely understood.

Vanadate stimulates DNA synthesis in fibroblasts, behaves as a growth factor mimetic agent promoting the transition of the cells.

Vanadium compounds have many applications in the therapeutic field, some of them are: treatment of diabetes, cancer, as well as it can be used as antiparasitic, antiviral and antibacterial.

## 1.5. Antioxidant activity of the oxovanadium(IV) complexes (chemical investigation)

The chemical studies revealed that oxovanadium(IV) complexesare capable of removing superoxide anion radical $O_2^{\bullet-}$ from the reaction environment [9].

Furthermore, it has been found that the complexes also scavenge stable organic radicals, such as 1,1-diphenyl-2-picrylhydrazyl radical (DPPH$^\bullet$) and 2,2'-azinobis(3-ethylbenzothiazoline-6 sulfonic acid) cation radical (ABTS$^{+\bullet}$)from a solution [10]. It is noteworthy that only carboxylate oxovanadium(IV) complexes show reactivity to DPPH$^\bullet$ and ABTS$^{+\bullet}$ radicals. Complex compounds of cobalt(II) and nickel(II), as well as free,

not bonded with a metal ion carboxylate ligands (and auxiliary ligands: phen and bpy) do not react with DPPH$^{\bullet}$ and ABTS$^{+\bullet}$ radicals.

Based on the chemical investigations, it has been shown that the selection of appropriate carboxylate ligands determines the antioxidant activity of complexes. Their activity is higher compared to the activity of a simple inorganic salt, oxidovanadium(IV) sulphate, VOSO$_4$. The oxydiacetateoxidovanadium(IV) complexes have a higher reactivity to the O$_2^{\bullet-}$ anion radical in comparison with the thiodiocetate complexes.

The results of investigations of antioxidant activity of carboxylate oxovanadium(IV) complexes open a new perspective of their use not only as substances exhibiting insulin-mimetic [11] or antineoplastic [12] activity, but also as compounds with promising cytoprotective properties against reactive oxygen species.

## 1.6.     Anti-diabetic activities of the oxovanadium(IV) complexes

Concerning applications of vanadium compounds as therapeutic agents, treatment of diabetes has been one of the main focuses. Medicinal applications of vanadium compounds have focused on their in vitro and in vivo activity in the treatment of insulin deficiency, type 1 diabetes (caused by destruction of pancreas $\beta$-cells), and insulin tolerance, type 2 diabetes, which is by far the more common form, frequently found with elderly people and increasingly also a problem for obese young people, stress or other environmental factors. The effects caused by vanadium compounds encompass the stimulation of glucose intake into cells (with successive degradation of glucose) and thus a lowering of the blood glucose level, the inhibition of glyconeogenesis and glycogenolysis, and the stimulation of lipogenesis (inhibition of lipolysis) [13].

In the treatment of diabetic animals and, sporadically, human individuals, V$^{5+}$ and V$^{4+}$ compounds have been employed. Mainly due to the very low oral bioavailability of inorganic salts (NaVO$_3$, VOSO$_4$) V$^{4+}$ complexes with organic ligands have been extensively explored. Organic ligands allow for a fine-tuning of the vanadium compound with respect to stability, rate of absorbance from the gastrointestinal tract (when applied orally), targeting of and internalization by the tissue cells, and toxicity. Among the compound tested as small molecule insulin-enhancers, VO(maltolato)$_2$ (BMOV) [14] and VO(Etmaltolato)$_2$ (BEOV) [15] have been extensively studied (Fig. 1). BMOV and BEOV may be taken orally and both lower plasma glucose levels in streptozotocin-induced (STZ) diabetic rats [16].
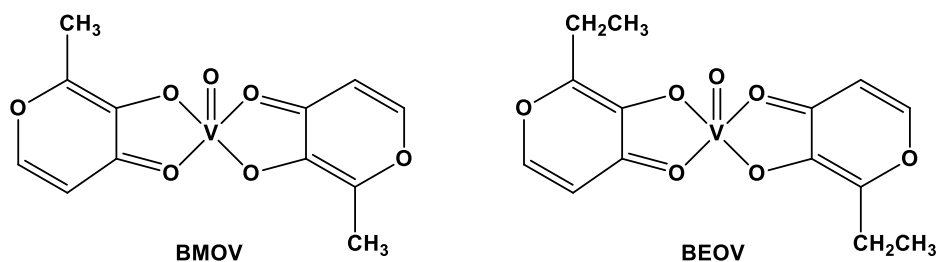
**Figure 10.** Schematic molecular structure of VO(maltolato)2 (BMOV) and VO(Etmaltolato)2(BEOV)

## 1.7.  Anticancer properties of the oxovanadium(IV) complexes

Vanadium compounds have been studied over the last few years because of their anti-cancer properties, but the mechanism of action of the compounds is still under study nowadays. The main targets for the antitumor effects of vanadium are the disruption of cellular metabolism and the alterations of cellular organelles such as lysosomes, mitochondria. Moreover, cell proliferation can also be disturbed by genotoxic effects of vanadium exerted at the nuclei of the cells and on DNA damage.

The interesting group of vanadium compounds are complexes of oxidovanadium(IV) with ligands that hold multiple donor atoms able to coordinate with metal centers. Strong chelating ligands are very important in living systems since they can facilitate the uptake and transport of metals inside the cells. Binary and ternary of oxodiacetate complexes of $VO^{2+}$, **[VO(oda)(H$_2$O)$_2$]**, **[VO(oda)(phen)]·1.5H$_2$O**and **[VO(oda)(bpy)]·H$_2$O** (where odadenates the oxodiacetate ion) [17], displayed important effects in bone related cells in culture (Figure 11) [18].
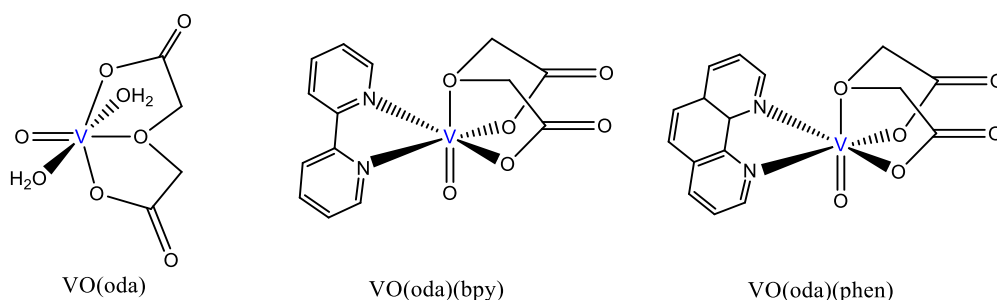


**Figure 11**. Structural formulas of VO-oda complexes

All these compounds were tested on two osteoblast-like cell lines in culture (MC3T3E1 derived from mouse calvaria andUMR106 derived from a rat osteosarcoma cells).

VO(oda) caused inhibition of cellular proliferation in both cell lines, but the cytotoxicity was stronger in the normal (MC3T3E1) than in the tumoral (UMR106) osteoblasts.

**[VO(oda)(H$_2$O)$_2$]** behaved as an inhibitory agent of osteoblast differentiation[19]. Moreover, **[VO(oda)(phen)]·1.5H$_2$O** in osteoblastic model caused inhibition of cellular proliferation in both cell lines (MC3T3E1 and UMR106), but the cytotoxicity was stronger in the normal than in the tumoral osteoblasts[20]. On the contrary, **[VO(oda)(bpy)]·H$_2$O** was statistically stronger in the tumoral cells [21]. **[VO(oda)(phen)]·1.5H$_2$O** caused strong cytotoxicity affecting lysosomes and mitochondria metabolism from the lowest tested dose, while **[VO(oda)(H$_2$O)$_2$]** and **[VO(oda)(bpy)]·H$_2$O** produced these effects at higher concentrations. No DNA damage could be detected by the comet assay with **[VO(oda)(H$_2$O)$_2$]**, while **[VO(oda)(phen)]·1.5H$_2$O** and **[VO(oda)(bpy)]·H$_2$O** induced DNA damage. Nuclease activity of the three compounds (Fig. 11) revealed that DNA cleavage caused by **[VO(oda)(bpy)]·H$_2$O** and **[VO(oda)(H$_2$O)$_2$]** was similar, while **[VO(oda)(phen)]·1.5H$_2$O** showed a stronger effect. Within these series of compounds, a good relationship between the bioactivity of the complexes and their structures is noticed. **[VO(oda)(phen)]·1.5H$_2$O** presented the most potent antitumor action in human osteosarcoma cells followed by **[VO(oda)(bpy)]·H$_2$O** and then by **[VO(oda)(H$_2$O)$_2$]** according to the number of intercalating heterocyclic moieties [22].

## 2. EXPERIMENTAL PROCEDURE

### 2.1.      Utilized  compounds

The following list contains the compounds that have been used during the experimental part of this project.

*Vanadyl acetylacetonate(VO(C$_5$H$_7$O$_2$)$_2$):* It is a powdered solid with a shine dark green colour. The compound that it is possible to find in the lab has a purity of 97.0%.

CAS: 3153-26-2

Its molecular weight is 265.16 g·mol$^{-1}$.

Melting point: 235 ºC.

Hazard statements: H302, H315, H319, H335.

Precautionary statements: P261, P305 + P351 + P338.

*Diglycolic acid (C$_4$H$_6$O$_5$):* The appearance of this compound is as white powderand it is not very compact. In the laboratory it is found the compound with a purity of 98%.

CAS: 110-99-6

Its molecular weight is 134.09 g·mol$^{-1}$.

Hazard Statements:H302, H315, H319,H335.

Precautionary statements: P261, P264, P270, P271, P280, P301+P312, P302+P352, P304+P340, P305+P351+P338, P312, P321, P330, P332+P313, P337+P313, P362, P403+P233, P405, and P501.

*1,10 –phenanthroline (C$_{12}$H$_8$N$_2$):* This compound looks like white powder.

CAS: 66-71-7

Its molecular weight is 180.21 g·mol$^{-1}$.

Melting point: 117ºC.

Hazard Statements: H301, H400, H410.

Precautionary statements: P264, P270, P273, P301+P310, P321, P330, P391, P405, and P501.

*2-amino-3-hydroxypyridine (C₅H₆N₂O):* It is a powdered solid with a grey-brown colour and it is not very compact. In the laboratory it is found the compound with a purity of 98%.

CAS: 16867-03-1

Its molar weight is 110.12 g·mol$^{-1}$.

Hazard Statements: H301, H302, H311, H315, H319, H335, H373.

Precautionary statements: P260, P261, P264, P270, P271, P273, P280, P301+P310, P301+P312, P302+P352, P304+P340, P305+P351+P338, P312, P314, P321, P322, P330, P332+P313, P337+P313, P361, P362, P363, P391, P403+P233, P405, and P501.

*2,2-bipirydyl (C₁₀H₈N₂)*: It is a solid that look as smalls white crystals.

CAS: 366-18-7

Its molecular weight is 156.18 g·mol$^{-1}$.

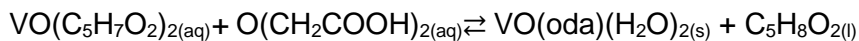Melting point: 70-72ºC.

Hazard Statements:H301 + H311.

Precautionary statements: P260,P280,P302 + P352,P308 + P310.

During experimental part they were employed as solvent water and ethanol.

## 2.2. Laboratry diary

### 2.2.1. Synthesis of VO(oda)(H₂O)₂

The synthesis of this reagent takes place following the next reaction:

$$VO(C_5H_7O_2)_{2(aq)} + O(CH_2COOH)_{2(aq)} \rightleftarrows VO(oda)(H_2O)_{2(s)} + C_5H_8O_{2(l)}$$

| n= 0.01 mol | n= 0.01mol | n= 0.01mol |
|---|---|---|
| m=2.65 g | m=1.34g | m=2.35g |

Note: The values of n are written in moles and m are written in grams

This synthesis stats measuring the beginning reactants in a 100mL round bottom flask.

In this case it is going to perform the synthesis of VO(oda) twice to determine which obtaining method is better, because this compound is going to be the beggining reactant for the rest of synthesis. The elimination of acetone shall be used as means of comparison.

In the first case it will be employed the rotator as elimination method and concentration the solution.

For the second case it will be used a reflux system to eliminate and concentrate.

In each case the needed amounts of reactants are measured, amount that is found in the reaction above.

After pouring both reactants in each flask , it is added deionized water to approximately to half of size (around 50mL in each case).

To the flask that will be employed for the rotator method, it is necessary to transfer the solution to a bigger flask because of technical reasons, since with a small size the flask does not  touch the water and the procedure will fail.

The highest temperature that will be necessary in rotator is 70ºC. In this process perform to removing one residue of the reaction, acetone, and concentrate of resulting solution.

When the tank temperature is 30ºC it is possible to observe the appearance of bubbles on solution.

An indicator that the elimination has ended, it is the color change from dark green to dark blue. This is because of the removed waste.

While the first solution is in the rotator, the reflux system is prepared, where the second solution is going to take part. A porous plate is deposited in the solution to avoid that the reaction takes place abruptly with liquid projection and get a continuous boiling.

Rotator

After 15 minutes working, the solution has disappeared almost totally, so it is added more deionized water to de flask  (50 mL approximately), because the solution continues to  be green.

After half an hour it is necessary the addition of more water because of the same reason explained above.

The intense dark blue solution is obtained after 50 min of working, where is found a precipitate with a color between blue and green. This precipitate will be filtrated after a rest time, around 30 min of wait, because appear more precipitate.

The solution is filtered by vacuum system, the precipitate is removed and the resulted solution is poured in a 100 mL round bottom flask, splitting 3 mL from the solution to later analysis (to know what it has been obtained in the synthesis).

Reflux

In this case, reflux system is built where the flask and a thermal blanket will be situated to perform the boiling of the solution.

After 15 min to the had been begun the experiment, the solution already  becomes dark blue, so the temperature of the  thermal blanket is reduced and it is maintained around 30 min.

After 50 min of reaction, the flask is removed from the reflux system with heating and it is allowed to rest until the flask gets cold.

The solutions are filtered because there could be any precipitate (nothing is observed during the filtration) and the obtained solution is poured in a 100 mL round bottom flask.

When the colors of two solutions are compared, It can clearly be seen how the colors of both do not look alike, being the solution 2 that is considered to be modified, since it has a dark blue color, but that being seen in backlight green shades are observed, considering in this way that the residue was not completely eliminated. Therefore the solution is subjected to the broken steam. While the solution is in the rotavapor, the color of the solution is compared with the color of solution 1. After approximately 1 hour in the rotator and an addition of water, the color obtained from the solution is close enough to the color of the solution. The first solution, so as to consider the reaction completed.

Three mililitres of the solution are separated for further analysis (to find out what It has been obtained after the reaction).

It is feasible that the reaction in the second case is not carried out with 100% of the reason that the temperature is lowered too soon and with less temperature the reaction does not "work", so the experiment it is repeated for the second time, controlling parameters as temperature and time, and it is continued with the vacuum filtration and drying crystals.

The solutions are filtered and the crystals are saved and let them get dry by air to evaporate the solvent.

The obtained crystals are a shining light blue.

Until the completion of the analysis I cannot conclude which of the two methods is more effective.

But after perform the experiment with both methods it is concluded that it will be used the reflux method because logistic reasons.

### 2.2.2. Synthesis of [VO(oda)(phen)]·1.5H$_2$O and [VO(oda)(bpy)]·H$_2$O

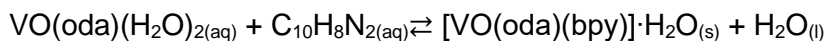To obtain these two compounds it will be used the one previouslysynthesized by rotator. Both syntheses are prepared in the same way

The reaction that takes place in first case:

$VO(oda)(H_2O)_{2(aq)} + C_{12}H_8N_{2(aq)} \rightleftarrows [VO(oda)(phen)] \cdot 1.5H_2O_{(s)} + H_2O_{(l)}$
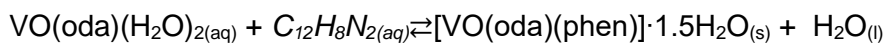
| n=0.01mol | n=0.01mol | n=0.01mol |
|-----------|-----------|-----------|
| m=2.35g | m=1.98g | m=3.97g |

And in the second case:

$VO(oda)(H_2O)_{2(aq)} + C_{10}H_8N_{2(aq)} \rightleftarrows [VO(oda)(bpy)] \cdot H_2O_{(s)} + H_2O_{(l)}$

| n=0.01mol | n=0.01mol | n=0.01mol |
|-----------|-----------|-----------|
| m=2.35g | m=1.56g | m=3.55g |

To obtain the both solutions of $VO(oda)(H_2O)_2$ are approximately 45 minutes in the reflux system and they are concentrated on the rotator.

Once obtained thecompoundsolid is poured in a flask where is added drop by drop the corresponding solution of phenantroline or bypiridin, previously prepared.

*[VO(oda)(phen)]·1.5H_2O*

The solution turns green as phenanthroline is added and it can be see how precipitate begins to appear. When practically all of the phenanthroline has been added, the solution becomes light green in color and more dense.

It is added deionizedwater till a partial dissolution of compound.

*[VO(oda)(bpy)]·H_2O*
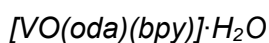
The solution turns green as the above obtained, but in this case after the totally addition of the bipyridine solution, there is not precipitate. Therefore the flask with the solution it is placed in the rotator till a brown solid begins to appear, due to the evaporation of the solvent.

When the concentration finish it is added water till the major part of solid adhered on the flask walls is dissolved and it is filtered by vacuum, obtaining small crystals (almost as powdered) with a shining brown color.

For both above cases the solutions are filtered to vacuum, the obtained precipitates are left for dry in the air and the solid are collected in a glass vials.

### 2.2.3. Synthesis of [VO(oda)(Hahp)]

To obtain this compounds it will be used the $VO(oda)(H_2O)_2$ previouslysynthesized by rotator. As in the above case the solution of 2-amino-3-hydroxypyridine (Hahp) is previously synthesized with a proportional amount to 0.01mol of the reactant (1.10g) and using ethanol as solvent.

The solution turns green as Hahp is added drop by drop slowly and it can be see how precipitate begins to appear and the solution becomes dark green in color. When the Hahp solution has added totally and the reaction ends, the flask is removed from the rotator, where the solution has been concentrated.

The solution is left to stand for about 30 minutes and is filtered under vacuum and the crystals obtained are left to dry in the air.

A bright dark green crystalline solid is obtained and crystals are poured in a glass vials.

### 2.3.        Efficiency of reactions

**Table 4.** Values to calculate the yield

| Compounds | Theoretical value[g] | Experimental value [g] |
|---|---|---|
| $VO(oda)(H_2O)_2$ | 2.35 | 1.47 |
| $[VO(oda)(phen)] \cdot 1.5H_2O$ | 3.97 | 3.43 |
| $[VO(oda)(bpy)] \cdot H_2O$ | 3.55 | 1.95 |

To calculate the yield of each reaction it has to divide the experimental value by the theoretical value, where it is obtained the next values:

$$Yield = \frac{experimental\ value}{theoretical\ value} \cdot 100$$

The next table contain all the values of yield obtained:

**Table 5.** Calculated values of yield

| Compounds | Yield |
|---|---|
| $VO(oda)(H_2O)_2$ | 62.55% |
| $[VO(oda)(phen)] \cdot 1.5H_2O$ | 86.4% |
| $[VO(oda)(bpy)] \cdot H_2O$ | 54.93% |

## 2.4. Characterization methods

### 2.4.1. Elemental analysis

It is a technique for determining the total content of carbon, hydrogen, nitrogen and sulphur present in a wide range of samples of organic and inorganic nature, both solid and liquid.

In this particular case is an inorganic compound consists of carbon, hydrogen and nitrogen.

This analytical technique is complementary to other structural analysis techniques for the confirmation of the molecular formula of compounds coming from organic or inorganic synthesis.

### 2.4.2. Uv-vis

Ultraviolet-visible spectrometry or UV-Vis spectrophotometry involves the spectroscopy of photons in the region of ultraviolet-visible radiation.

This technique deals with transitions from the excited state to the basal state, while absorption spectrometry measures transitions from the basal state to the excited state.

In this region of the electromagnetic spectrum, molecules undergo electronic transitions.

UV/Vis spectrometry is commonly used in the quantitative determination of transition metal ion solutions and highly conjugated organic compounds. In this case, the technique will be used in the analysis of transition metal ion solutions.

Transition metal ion solutions can be colored (i.e., they absorb visible light) because electrons in metal atoms can be excited from one electronic state to another. The color of metal ion solutions is greatly affected by the presence of other species, such as some anions or ligands.

For the particular case concerning this experimentation, the following theoretical data have been obtained on the transitions that take place in the synthesized compounds: the lower energy bands of VO(oda)bpy (855nm)was assigned to the $b_2 \rightarrow e$ transition, the band at 650nm was assigned to the $b_2 \rightarrow b_1$ transition, whereas the other one,

found at 440nm could be assigned to the $b_2 \rightarrow a_1$ transition. For VO(oda)phen, the two lower energy bands were assigned to the $b_2 \rightarrow e$ (820nm) and $b_2 \rightarrow b_1$ (580nm) transitions, whereas the one, found at 450nm could be assigned to the $b_2 \rightarrow a_1$ transition. In the precursor complex, VO(oda), the first two $d \rightarrow d$ transitions were observed at 792 and 618 nm, respectively. [ FIG X]
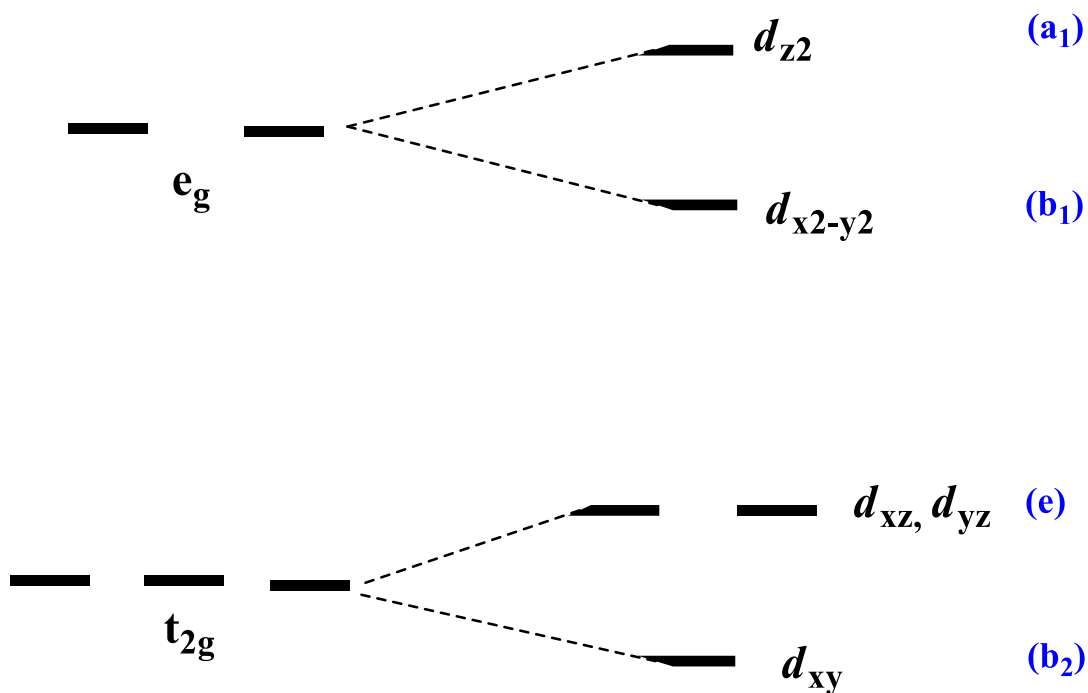
$d_{z2}$ (a₁)

$e_g$

$d_{x2-y2}$ (b₁)

$d_{xz}, d_{yz}$ (e)

$t_{2g}$

$d_{xy}$ (b₂)

**Figure 12. The d-orbital diagram in an octahedral crystal field. The effect of an distorted octahedral crystal field on the energies of d orbitals.**

In Figure X I presented a diagram of energy levels $e_g$ and $t_{2g}$ in a deformed octahedral complex type [VO(oda)(H$_2$O)$_2$]. Analysis of the diagram indicates that the absorption band located at 790 nm corresponds to the electron transfer from $d_{xy}(b_2)$ orbital to $d_{xz}$ orbital (or $d_{yz}$) (e), while the band at higher energy (610 nm) passes through $d_{xy}(b_2) \rightarrow d_{x2-y2}$ (b₁).

### 2.4.3. Infrared

Infrared spectrometry (spectroscopy IV) is a type of absorption spectrometry that uses the infrared region of the electromagnetic spectrum.

Infrared spectrometry is based on the fact that the chemical bonds of substances have specific vibration frequencies, which correspond to the energy levels of the molecule.

These frequencies depend on the shape of the potential energy surface of the molecule, the molecular geometry, the atomic masses and possibly the vibrational coupling.

The data obtained from the bibliography for spectrum analysis are described in the following section on "data treatment" along with the experimentally obtained spectra.

IR spectroscopy covers a wide region (12800-1000 cm-1).

The absorption of radiation in the IR region can give information about the nature of compounds, the existence or not of functional groups and the structure of molecules.

The region of the IR is divided into:

- Near IR: 12800-4000 cm-1
- Mid IR: 4000-280 cm-1
- Far IR: 200-10 cm-1

In the experimental field, the sub-region that is most used is that of the medium IR and therefore, although it is often not specified, we speak of the medium IR.
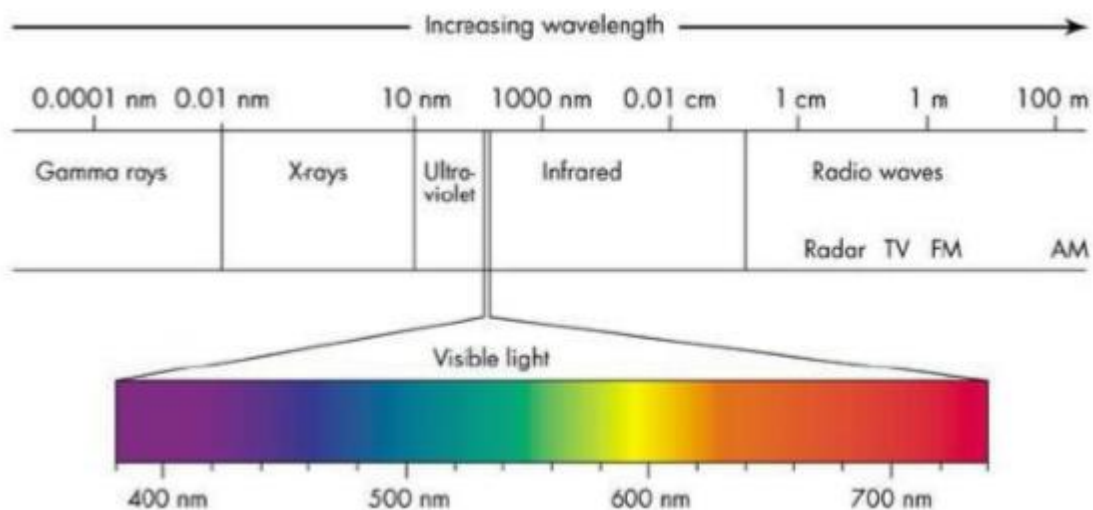


**Figure 13.** Diagram od the spectrum distribution of wavelength

### 2.4.4. Termogravimetric analysis

Thermogravimetric analysis (TG) is widely used with DSC, TMA and DMA. TG measures the mass of a sample while the sample is heated or cooled in a defined atmosphere. TG is mainly used for characterization of materials with regard to their composition.

A TG/DSC instrument allows you to measure even thermal events that do not cause a mass change, such as melting, glass transition or other solid-solid phase transitions.

Thermogravimetric analysis (TG) is used to characterize the physical and chemical properties of materials as a function of temperature in a precisely controlled atmosphere.

The analysis and treatment of the spectra will be realized in the next section.

### 2.4.5. Antioxidant properties

Antioxidants are substances that can prevent or slow damage to cells caused by free radicals, unstable molecules that the body produces as a reaction to environmental and other pressures. They are sometimes called "free-radical scavengers".

Antioxidants are substances that can prevent or slow damage to cells caused by free radicals, unstable molecules that the body produces as a reaction to environmental and other pressures.

They are sometimes called "free-radical scavengers".

Free radicals are waste substances produced by cells as the body processes food and reacts to the environment. If the body cannot process and remove free radicals efficiently, oxidative stress can result. This can harm cells and body function.

Compounds with antioxidant properties are substances that have the property of neutralizing free radicals, reducing oxidative damage and thus preventing or delaying the emergence of various diseases. complex diagnosis.

There are several methods for the determination of this property, but in the case study the ABTS method is used.

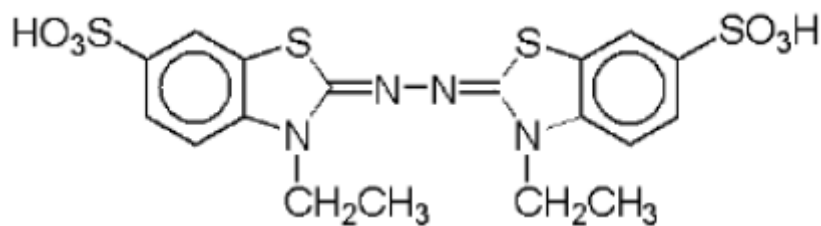ABTS is the acronym of 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid).



**Figure 14.** Structure of the ABTS 1

With the ABTS you can evaluate the activity of compounds of nature

hydrophilic and lipophilic, the ABTS has to be generated after a chemical, enzymatic or also a chemical reaction. Electrochemistry. The ABTS radical also has the advantage that its spectrum presents maximum absorbance at 414, 654, 754 and 815 nm in alcoholic medium.

Ascorbic acid shall be used as the reference compound, and a comparison shall be made as to whether the synthesised compounds have better or worse antioxidant properties than the reference compound.

## 2.5. Devices used during the characterization

**Elemental analysis**

Vario EL analyzer Cube CHNS

**IR spectra**

BRUCKER IFS 66 spectrophotometer

**Thermal analysis**

Netzsch TG 209 apparatus coupled with a Bruker IFS 66 spectrometer

NetzschSTA 449 *F3 Jupiter*® thermal analyzer

**UV-Vis spectra**

Perkin-Elmer Lambda 650 double beam spectrophotometer

# 3. RESULTS AND DATA TREATMENT

## 3.1. Elemental analysis

The composition of the compounds studied, namely **[VO(oda)(H₂O)₂]**, **[VO(oda)(phen)]·1.5H₂O** and **[VO(oda)(bpy)]·H₂O** were established on the basis of the elemental analysis of carbon, hydrogen and nitrogen (Vario EL analyzer Cube CHNS). The results I have shown below:
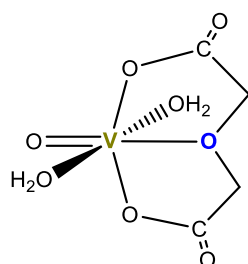
1. *[VO(oda)(H₂O)₂]*        M = **234.94** [g/mol]



**Figura 15.** The structure of [VO(H2O)2]

**Table 6.** Data of elemental analysis

| Compound | Experimental | | Calculated | |
|---|---|---|---|---|
| | C [%] | H [%] | C [%] | H [%] |
| **[VO(oda)(H₂O)₂]** | 20.31 | 3.47 | 20.44 | 3.44 |

2. *[VO(oda)(phen)]·1.5H₂O*        M = **406.00** [g/mol]
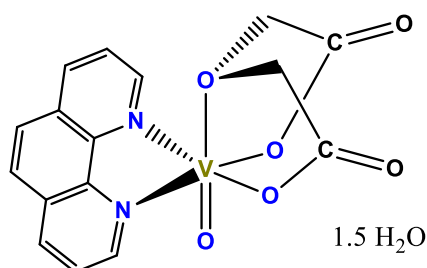


**Figura 16.** Structure of [VO(oda)(phen)]·1.5H2O

**Table 7.** Data of elemental analysis

| Compound | Experimental | | | Calculated | | |
|---|---|---|---|---|---|---|
| | C [%] | H [%] | N [%] | C [%] | H [%] | N [%] |
| **[VO(oda)(phen)]·1.5H$_2$O** | 47.11 | 3.73 | 6.86 | 47.29 | 3.69 | 6.90 |

**3.** *[VO(oda)(bpy)]·H$_2$O*     M = **372.94** [g/mol]
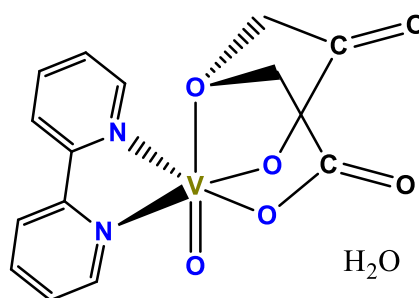


**Figura 17.** Structure of [VO(oda)(bpy)]·H2O

**Table 8.** Data of elemental analysis

| Compound | Experimental | | | Calculated | | |
|---|---|---|---|---|---|---|
| | C [%] | H [%] | N [%] | C [%] | H [%] | N [%] |
| **[VO(oda)(bpy)]·H$_2$O** | 44.98 | 3.80 | 7.49 | 45.05 | 3.75 | 7.51 |

Based on the results of elemental analysis, it can be noticed that the percentage of elements determined on the basis of the compound formula (see above) is in accordance with the results obtained by the experimental method. The results confirm the correctness of the summary formula of the compounds and indicate on the purity of the synthesized complexes.

### 3.2.   UV-Vis analysis

In Figure 18 I have presented the spectrum of an aqueous solution of $[VO(oda)(H_2O)_2]$ at concentrations of 0.2mM.

Due to the fact that the oxovanadium(IV) ion has one valence electron in orbital *d* (vanadium (IV) electron configuration: $[Ar]\ 3d^1$), the presence of the absorption band on the UV-Vis spectrum (Figure 18) is a consequence of the electron transfer within *d* orbitals, whose energy was degenerated under the influence of the field of ligands caused by the presence of the $oda^{2-}$ and $H_2O$ ligands as well as the *oxido* ligand ($O^{2-}$) in the coordination sphere of V(IV). The characteristic maxima of absorption on the Vis spectrum of the test compound is found at 790 nm and 610 nm for $[VO(oda)(H_2O)_2]$ (the compound on which the data analysis was carried out).
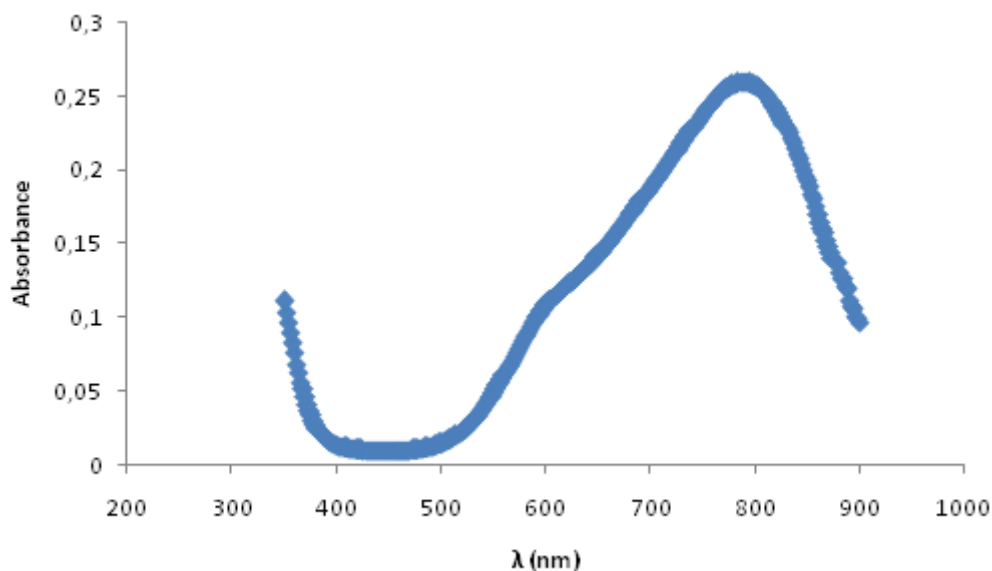


Figure 18. The UV-Vis spectrum of $[VO(oda)(H_2O)_2]$ (concentration 0.2mM)

Considering the data obtained experimentally, with the measurement of solutions of VO(oda)(H2O) at different concentrations, it has been possible to determine that in the spectra observed below there are 2 absorption maximums, one at 790 and the other at 610.
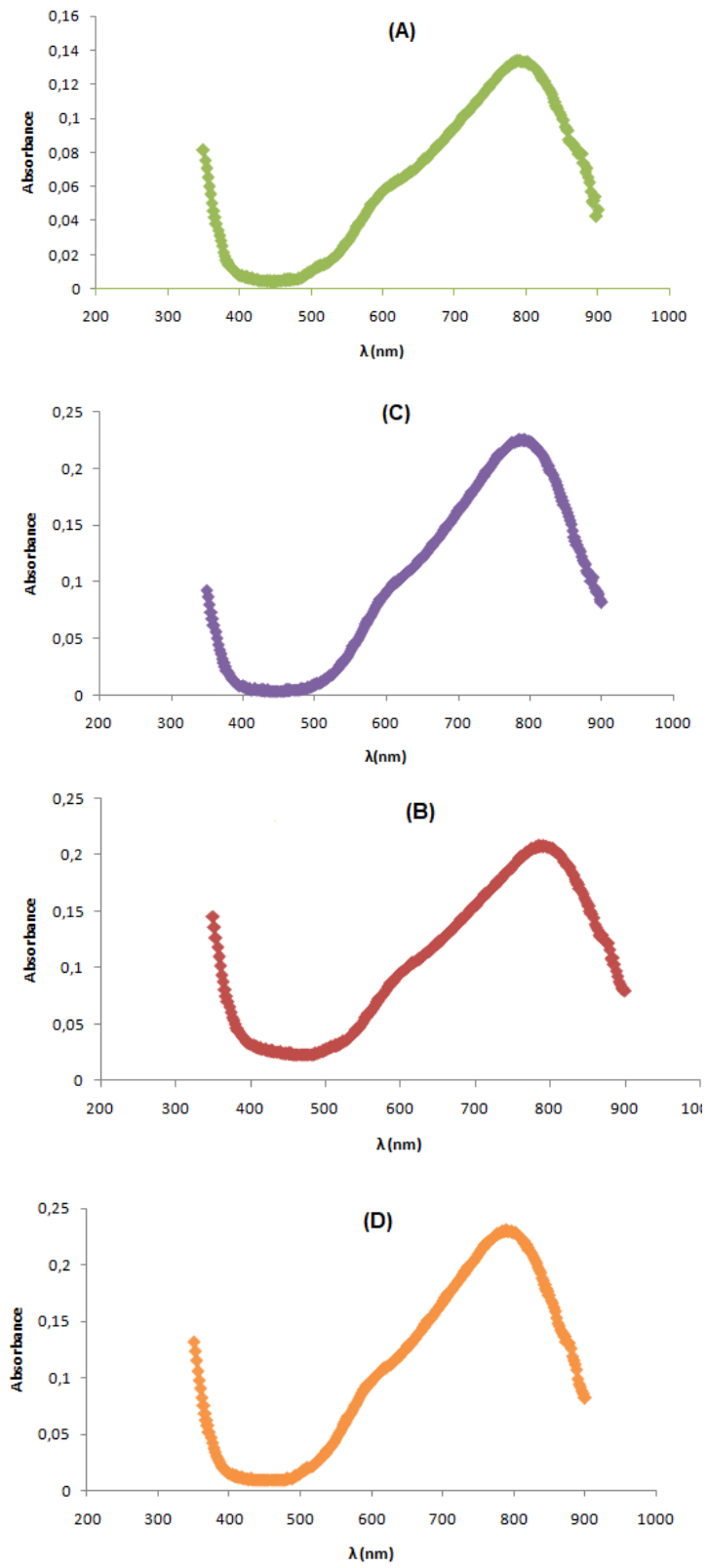
**Figure 19**. UV-Vis spectra with different concentration [VO(oda)(H2O)2] according to: (A) [1:1], (B) [1.5:0.5], (c) [1.75:0.5] by reflux and (D) [1.75:0.5] by rotator.

Starting from this premise, the calculation of evsilon is made for each of the observed maximums, using Beer-Lambert's law for its determination:

$A = \varepsilon \cdot l \cdot c$

Where:

l=cell thickness                    ε=mola aborptivity

c=concentration                   A=absorbance

**λ = 790 nm**

**Table 9**. Necessary data to obtain the graphic

| [] | Absorbance |
|---|---|
| 0.01 | 0.2596 |
| 0.00875 | 0.225131 |
| 0.0075 | 0.207964 |
| 0.005 | 0.133508 |
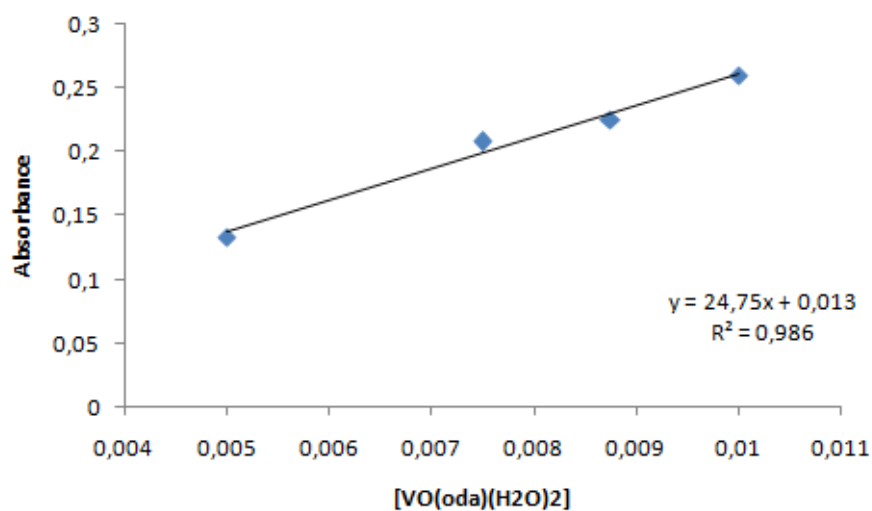


**Figura 20. Graph for the calculation of molar absorptivity at the maximum wavelength of 790nm**

**Table 10**. Values of calculated molar absorption

| ε 1 | 25.960 |
|---|---|
| ε 2 | 25.729 |
| ε 3 | 27.729 |
| ε 4 | 26.702 |
| ε (790nm) | 26.530 |

The obtained equation gives it the value of ε which is the slope of the equation hence ε=24.75

**λ= 610nm**

**Table 11.** Necessary data to obtain the graphic

| [] | Absorbance |
|---|---|
| 0.01 | 0.11569 |
| 0.00875 | 0.097876 |
| 0.0075 | 0.10071 |
| 0.005 | 0.0607 |
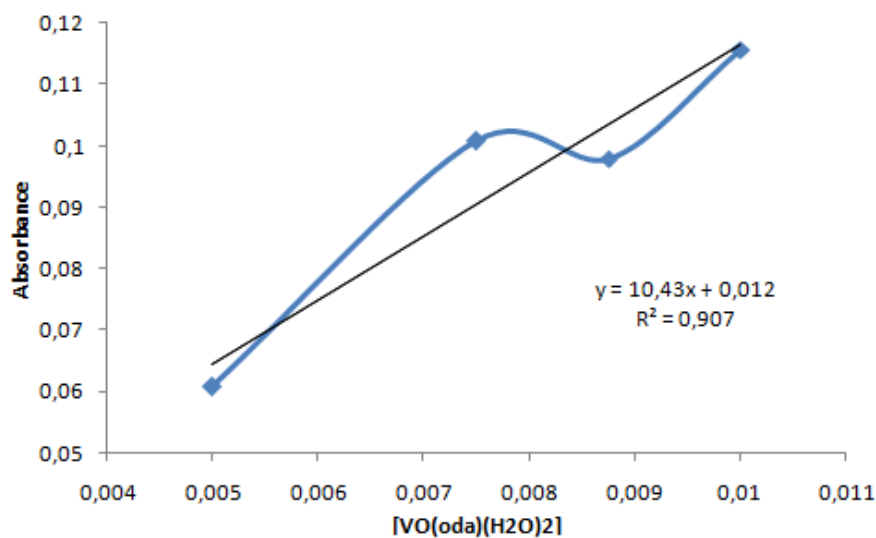


**Figura 21. Graph for the calculation of molar absorptivity at the maximum wavelength of 610 nm**

**Table 12.** Values of calculated molar absorption

| ε 1 | 11.569 |
|---|---|
| ε 2 | 11.186 |
| ε 3 | 13.428 |
| ε 4 | 12.140 |
| ε (610nm) | 12.081 |

The obtained equation gives it the value of ε which is the slope of the equation hence ε=10.43.

### 3.3. Infrared analysis

To procedure the infrared analysis it is necessary know each specific group or link that appear and at what wavelength should they appear in the infrared region.

For this reason below it can be find a table with the different wavelengths and the range of them:

|          | VO(oda)(H$_2$O)$_2$ | VO(oda)(bipy) | VO(oda)(Hahp) |
|----------|---------------------|---------------|---------------|
| v(VO)    | 994                 | 994           | 999           |
| v(COO)   | 1424-1590           | 1666          | 1678          |
| v(OH)    | 3056-2887           | 3551-3422     |               |
| v(COC)   | 1136                |               |               |
| v(NV)    |                     | 310-400       | 310-400       |

*In the case of the range of COO, these wavelength including the symmetric and the asymmetric vibration.*

In the following images are finding the spectra of each compound synthesized during the experimental process:
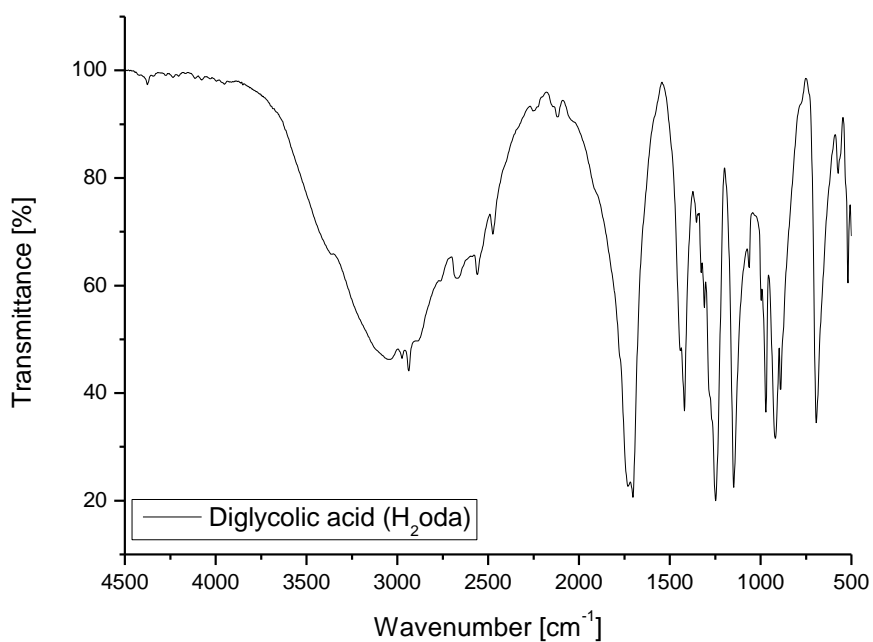


**Figura 22.** IR spectrum of H2oda

This spectrum belongs to one of the beginning reactants of the synthesis. The reactant which gives the "oda" ligand to the complex.
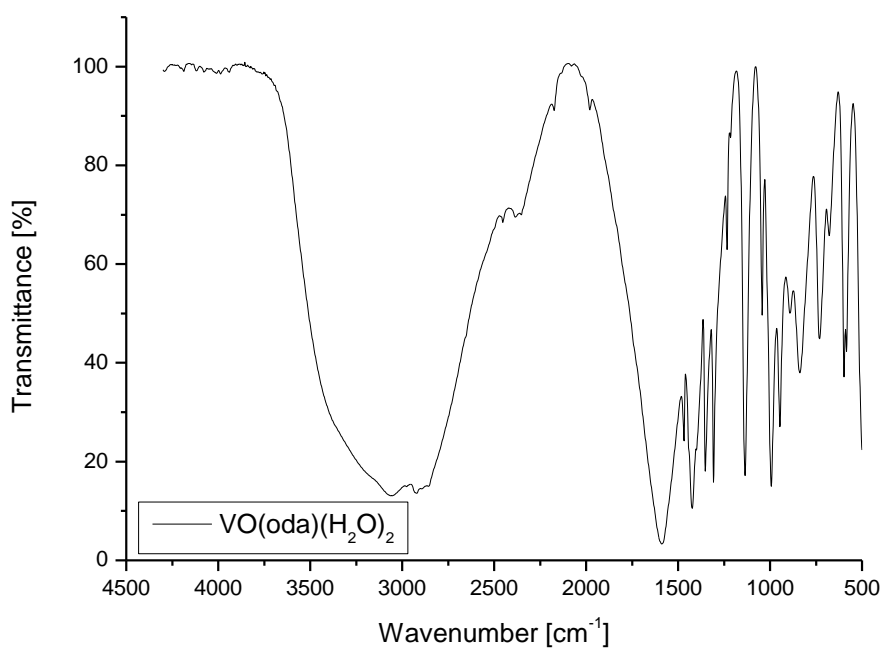


**Figura 23.** IR spectrum of [VO(oda)(H2O)2]

In this case the spectrum gives the characteristic peaks of the principal compound, which is the starting compound for the other synthesized compounds.

The next spectra belong to [VO(oda)(bpy)]·$H_2O$ and [VO(oda)(Hahp)] respectively.
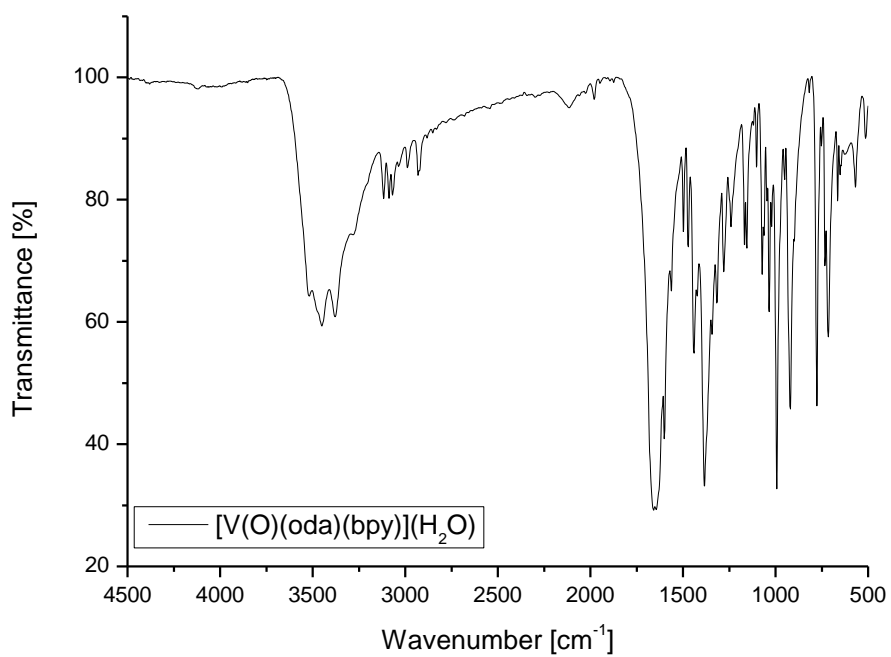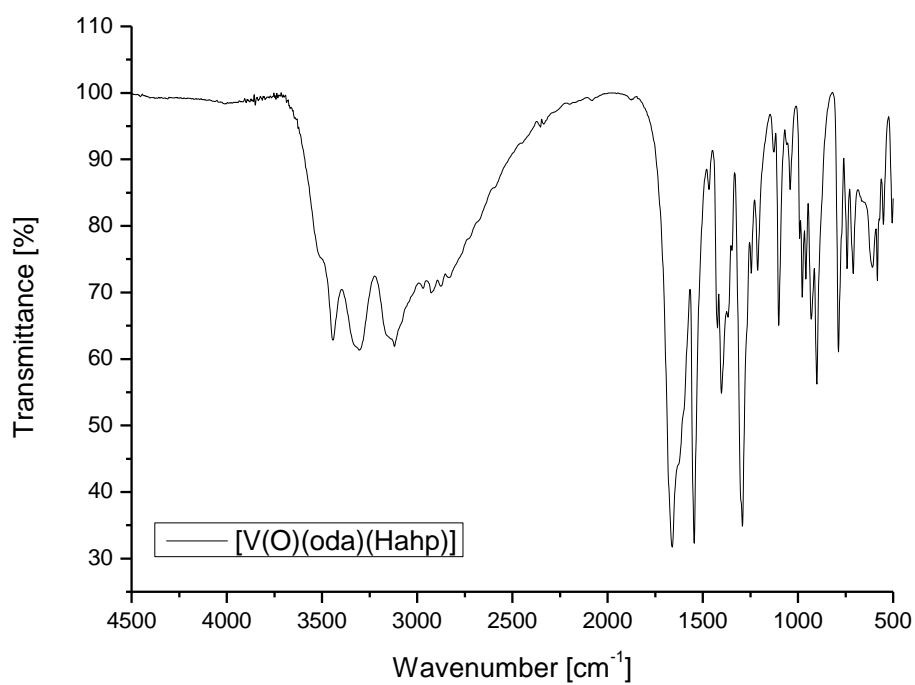
**Figura 24.** IR spectrum of [VO(oda)(bpy)]·H2O



**Figura 25.** IR spectrum of [VO(oda)(Hahp)]

### 3.4. Thermal analysis

In order to determine the thermal properties of the tested compounds, namely [VO(oda)(H$_2$O)$_2$], [VO(oda)(phen)]·1.5H$_2$O and [VO(oda)(bpy)]·H$_2$O, I used a thermogravimetric technique combined with the analysis of volatile decomposition products TG-FTIR. Additionally, I also investigated thermal properties of 2,2'-oxydiacetic acid (H$_2$oda).

**Thermal decomposition of 2,2'-oxydiacetic acid (H$_2$oda)**

In Figure 26, I presented the thermogravimetric curve (TG) of the thermal decomposition process of 2,2'-oxydiacetic acid (H$_2$oda) under argon atmosphere.
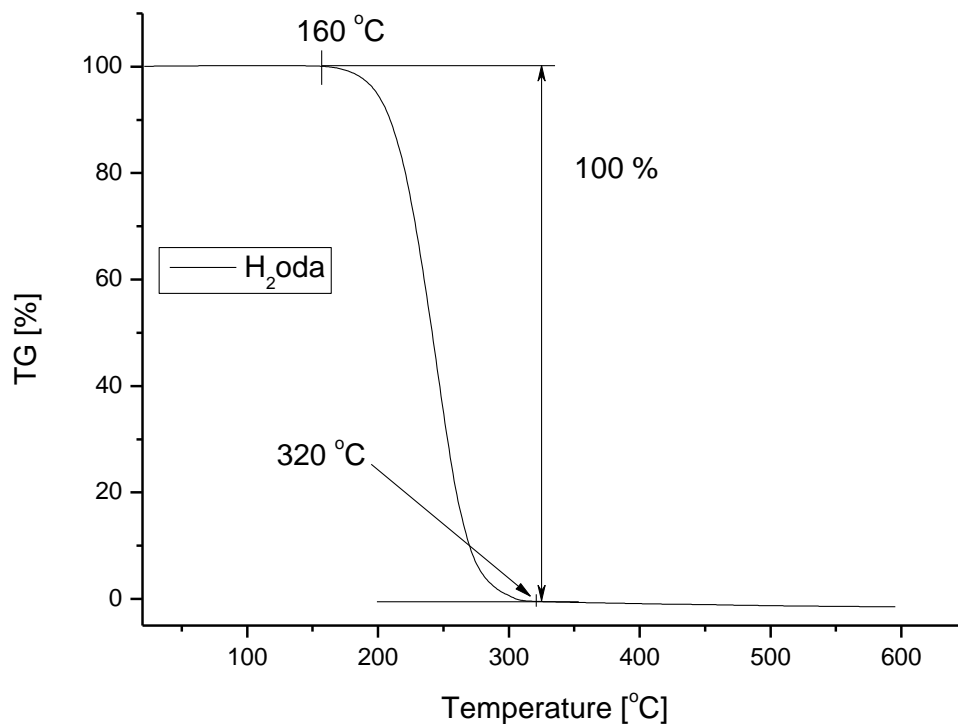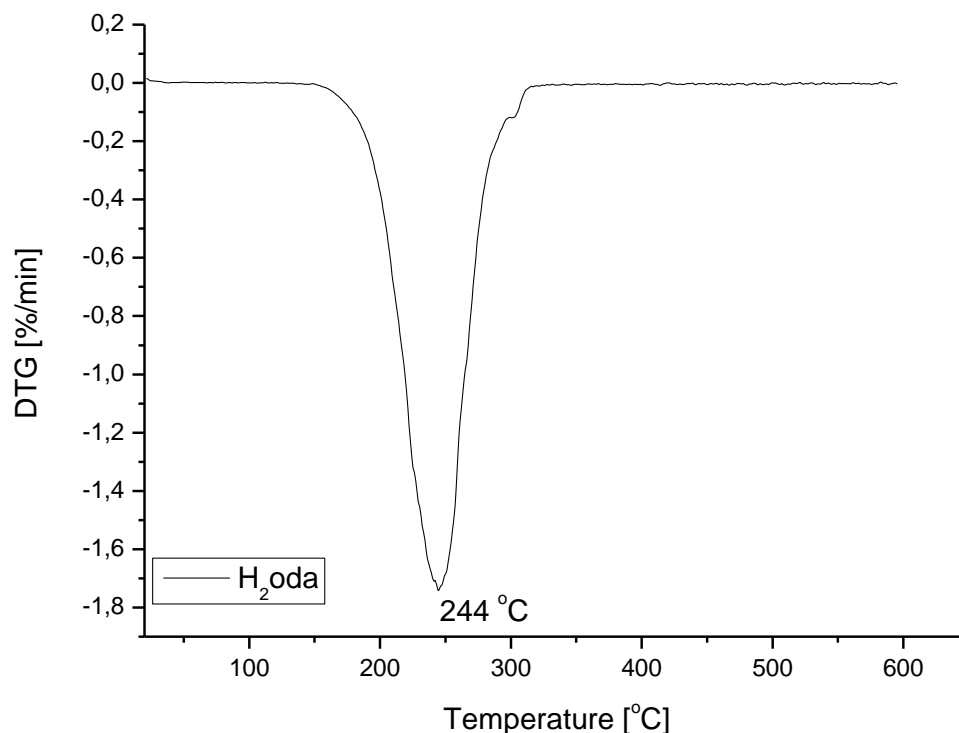


**Figure 26**. TG curve of the thermal decomposition of H2oda in Argon

The decomposition of H$_2$oda begins at a temperature of about 160 oC and proceeds in one step. Under the experimental conditions, thermal decomposition of the acid is the fastest at 244 oC, as evidenced by the maximum on the DTG curve (Figure

27). At a temperature of approx. 320 oC, the total weight loss of the sample occurs (about 100%).



**Figure 27.** DGT curve of the thermal decomposition of H2oda in Argon

In Figure 28 I presented the IR spectrum of volatile products of thermal decomposition of H2oda. On the IR spectrum in the range 4000 - 3500 cm-1 and 1550 - 1300 cm-1 absorption bands characteristic for water are present. Their presence is related to the initial dehydration of the acid leading to the formation of diglycolic anhydride. Vibration bands confirming the presence in the volatile decomposition products of acid anhydride are located at 1838 cm-1 [$v_{as}$(C-O)], 1750 cm-1 [$v_{as}$ (C-O)], 1200 cm-1, 1087 cm-1 and 958 cm-1 [v(C-O)] (Fig. 28.). The diglycolic anhydride is unstable and undergoes decarboxylation leading to the formation of CO and $CO_2$(Fig. 28.). On the basis of the TG-FTIR analysis, I proposed a pathway of thermal transformation of $H_2$oda (Fig. 29.).
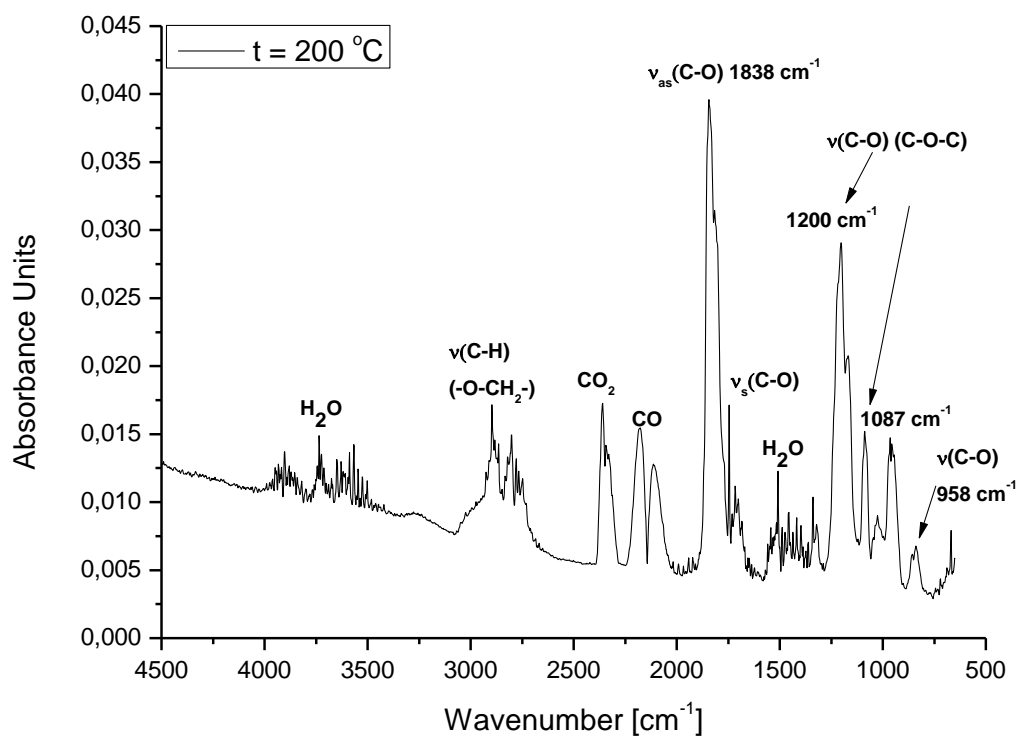
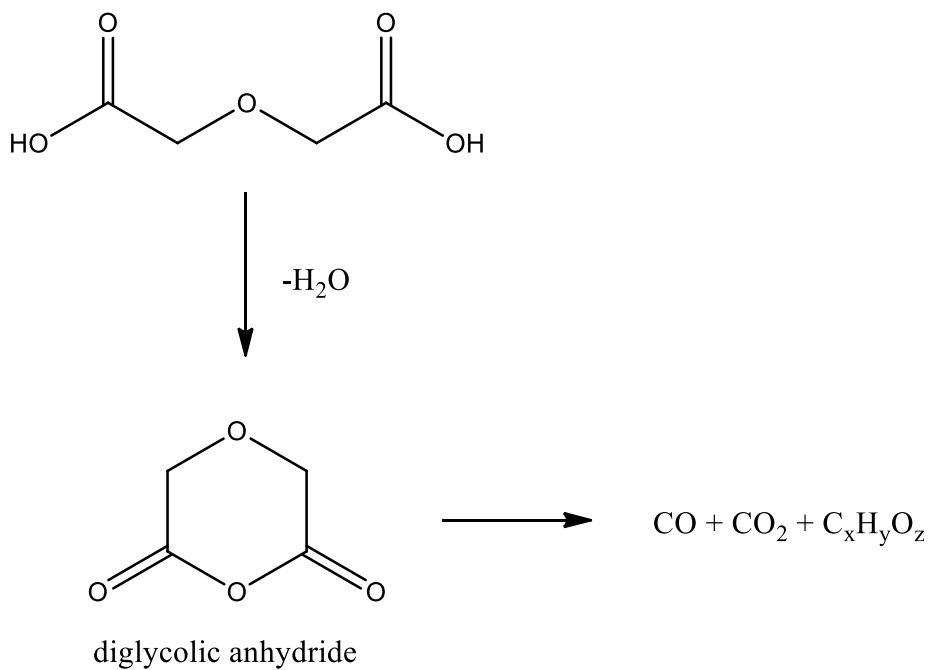**Figure 28.** IR spectrum of volatile decomposition products of H2oda released at 200ºC in Argon



diglycolic anhydride

**Figure 29.** Scheme of thermal transformations of H2oad in Argon atmosphere

## Thermal decomposition of [VO(oda)(H₂O)₂]

In Figures 21 and 22, I presented the thermogravimetric curves of the thermal decomposition of **[VO(oda)(H₂O)₂]** under argon atmosphere (Fig. 21) and in the synthetic air (Fig. 22), respectively.
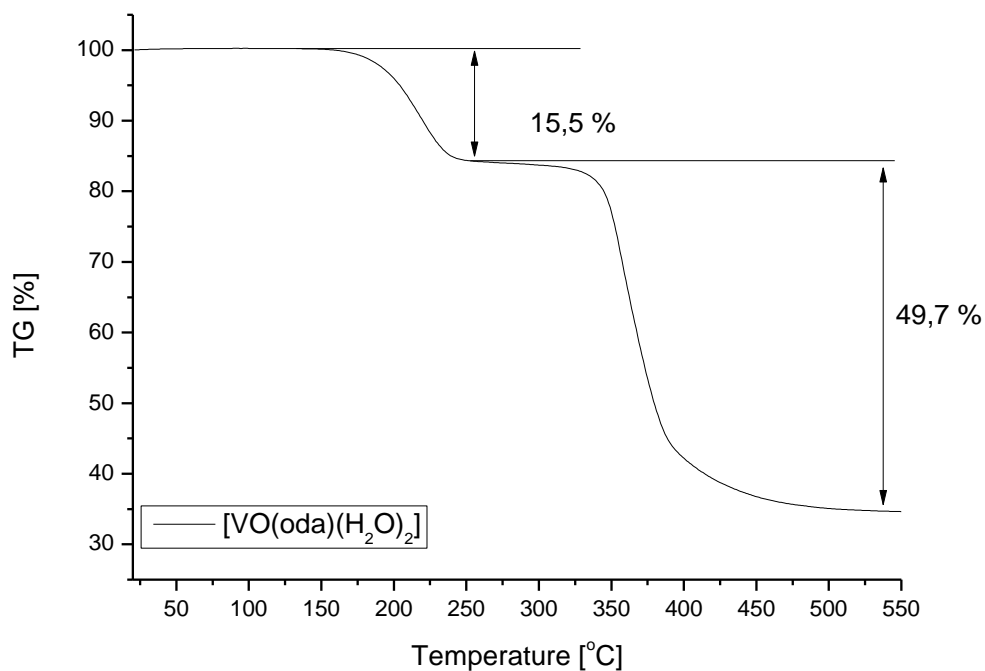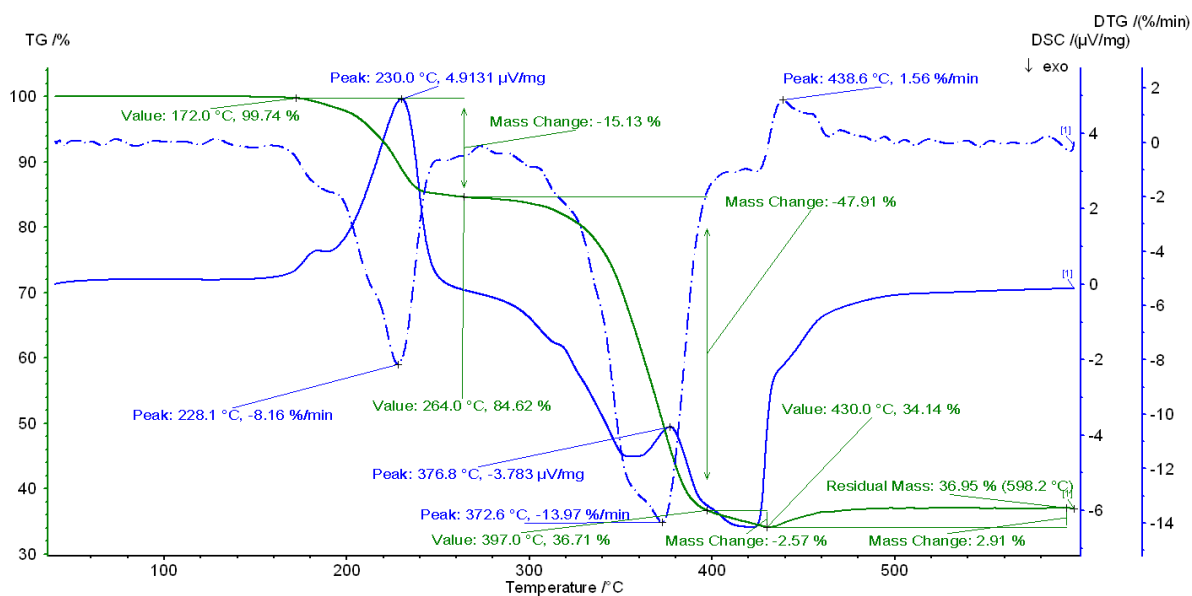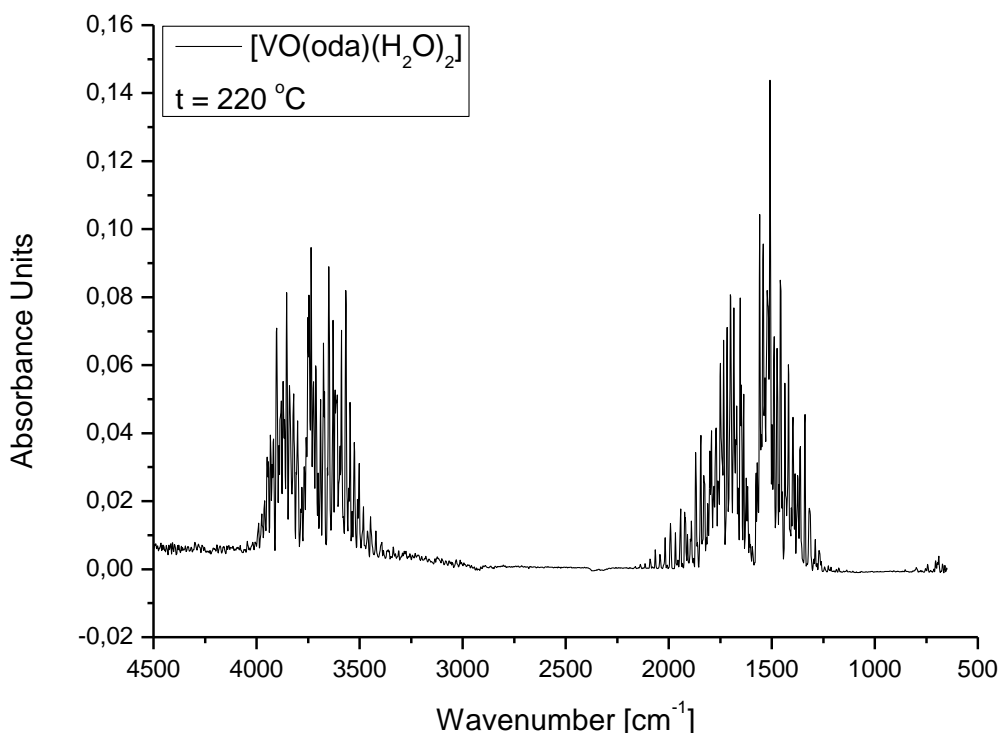


**Figure 30**. TG curve of thermal decomposition of [VO(oda)(HaO)2] in Argon



**Figure 31.** TG, DTG and DSC curves of thermal decomposition of [VO(oda)(H2O)2] in the synthetic air.

As seen (Figs. 30 and 31), thermal decomposition of **[VO(oda)(H₂O)₂]** consists of two main stages. The first one starts at ca. 170 oC and comes to an end at ca. 265 oC. The decomposition of the sample is not preceded by melting, as there are no thermal effects on the DSC curve below 170 oC. The atmosphere (Ar or synthetic air) of the thermal decomposition of **[VO(oda)(H₂O)₂]** does not influence the first decomposition step.

The first step (170 - 265 °C) corresponds to the loss of the coordination water (the two aqua ligands). This is demonstrated by a 15.6% mass loss (in the TG curve) close to 15.3% as calculated for the loss of two water molecule, as well as by IR bands over the 4000–3500 and 1750–1400 cm$^{-1}$ ranges assignable to the water vapour (Fig. 32).



**Figure 32.** The IR spectrum of the volatile preducts of thermal decomposition of [VO(oda)(H2O)2] in argon ar 220ºC.

Thermal dehydration of **[VO(oda)(H₂O)₂]** is the fastest at ca. 228 °C (the mass loss 8%/min), as evidenced by the maximum on the DTG curve (Figure 31).In Figure 33 I showed the scheme of the dehydration process of **[VO(oda)(H₂O)₂].**
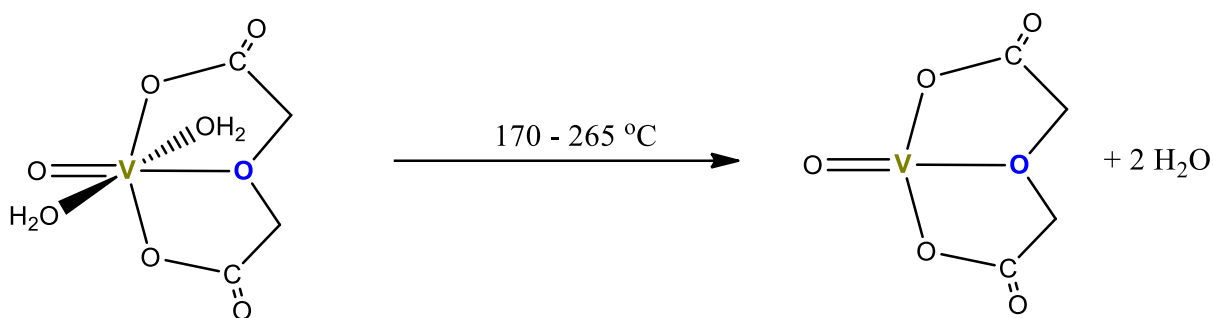
**Figure 33**. Dehydration of [VO(oda)(H2O)2]

The second step is rapid with onset around 265 oC. The DTG curve indicates that at 373 oC the rate of the mass loss equals ca. 14 %/min. Inspection of the IR spectra of gaseous decomposition products released over the temperature rage considered (265 - 550 oC) indicates that the decompositionof the anhydrate compound**[VO(oda)]** is a complex process leading throughdecarboxylation reactions to differentintermediate products (Fig. 34).
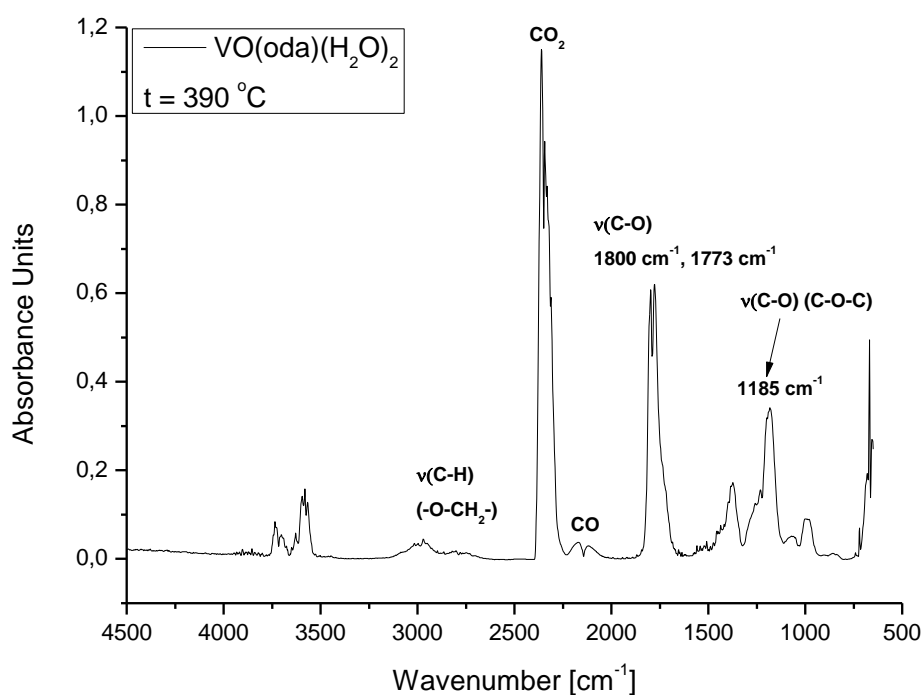


**Figure 34.** The IR spectrum of the volatile products of thermal decomposition of [VO(oda)(H2O)2] in Argon at 390ºC.

The residual mass of the products of thermal decomposition of **[VO(oda)(H₂O)₂]** in argon at 550 °C suggests the formation of vanadium(IV) oxide, $VO_2$.The residual mass found based on the TG curve analysis is 34.8%, whereas calculated for $VO_2$ (m = 82.94 u) equals 35.6%.

A different situation is seen during the thermal decomposition of **[VO(oda)(H₂O)₂]** in the synthetic air. At 430 °C the residual mass of the sample suggests the formation of the $VO_2$, as it is in the case of the decomposition of the **[VO(oda)(H₂O)₂]** compound in argon. However, above 430 oC a slightly increase of the sample mass is observed (ca. 3%) (Fig. 31). This phenomenon is probably due to the interaction of the solid product of the thermal transformation of **[VO(oda)(H₂O)₂]**, namely $VO_2$ with oxygen that is the component of the atmosphere (synthetic air) under which the decomposition occurs:

$$4 \; VO_2 + O_2 = 2 \; V_2O_5$$
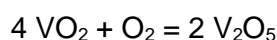
Thus, it can be concluded that the type of the atmosphere, oxidative (synthetic air) or ambient (argon) does not affect the dehydration of the **[VO(oda)(H₂O)₂]** but has impact on the final product of the thermal decomposition. The general scheme of the thermal decomposition of **[VO(oda)(H₂O)₂]**inthe synthetic air and in argon is presented in Figure 35.



**[VO(oda)(H₂O)₂]**

Synthetic air or Argon     170 - 265 °C

**[VO(oda)] + 2 H₂O**

Synthetic air                 Argon

265 - 430 °C                  265 - 550 °C

**$VO_2$ + a CO + b $CO_2$ + $C_{(x-a-b)}H_yO_{(z-a-2b)}$**

**$VO_2$ + a CO + b $CO_2$ + $C_{(x-a-b)}H_yO_{(z-a-2b)}$**

430 - 550 °C    + $O_2$

**$V_2O_5$**

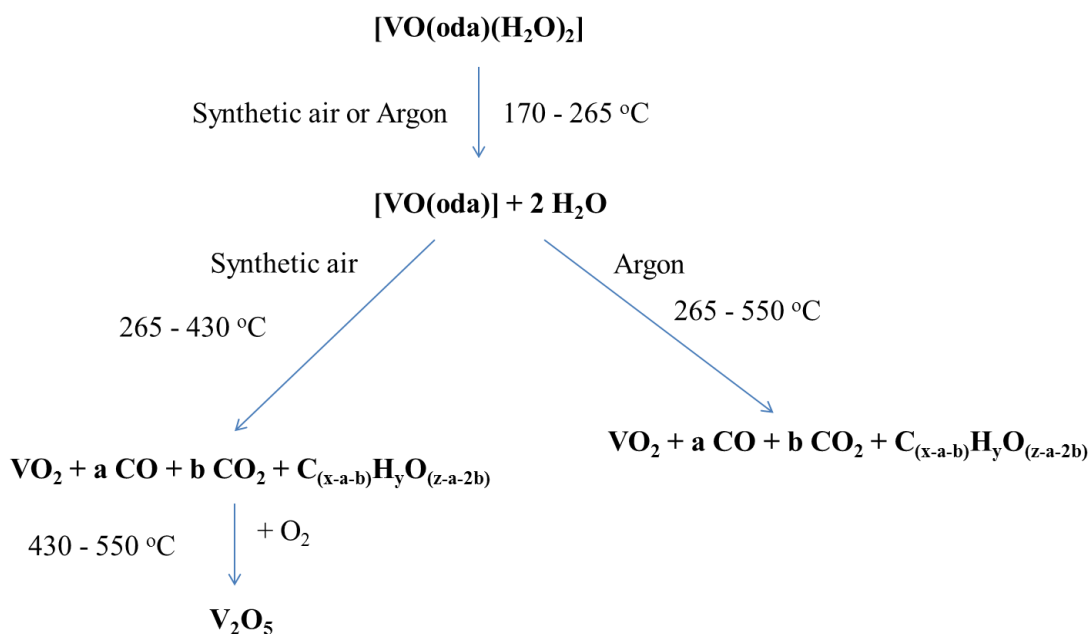**Figure 35.** The scheme of thermal decomposition of [VO(oda)(H2O)2] in the synthetic air in Argon

### 3.5. Antioxidant properties

Based on the solutions previously prepared for the UV-Vis measurements, the corresponding solutions are prepared for the study of the antioxidant properties of the VO(oda)(H2O)2 and VO(oda)(bpy) complexes.

The starting solution of the first complex has a concentration of 5 mmol while the concentration of the second complex is 10 mmol. We have to prepare a solution with a concentration of 0.16 mmol.

Once the solutions have been prepared, we proceed to determine if the concentration is adequate for the determined wavelength and if not, dilute or concentrate it until it adapts to the range we have set.

When mixing for the different measurements, let them stand for 5 minutes, which is the reaction time.

The dissolution of ABTS is an intense dark green that during these 5 minutes the dissolutions must become colourless (the more colourless they are, the more antioxidants they are).

Samples if diluted to a concentration of 0.08 mmol

Dilute again to a concentration of 0.04 mMol

This test compares whether synthesized compounds are better or worse antioxidants than ascorbic acid.

**Table 14.** Data of ABTS + VO(oda)(H2O)

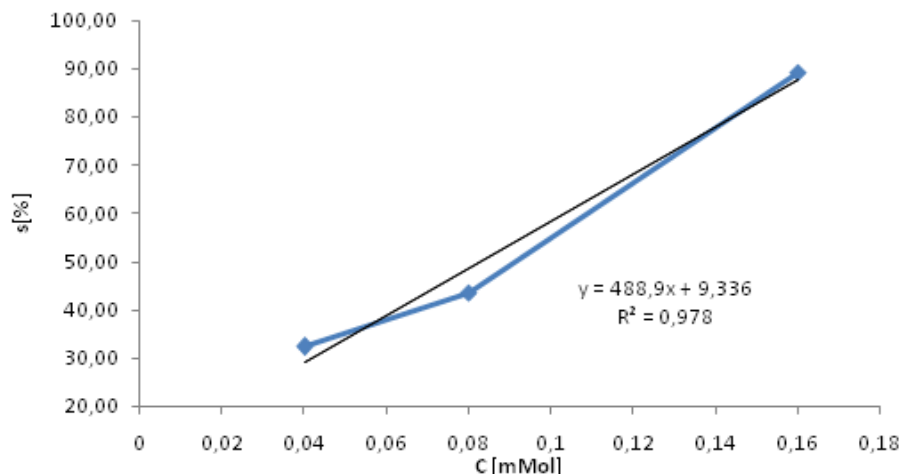| Absorbance | c[mMol] | S [%] |
|:---:|:---:|:---:|
| 0.19 | 0.16 | 89.24 |
| 0.68 | 0.08 | 43.45 |
| 0.8 | 0.04 | 32.23 |

**Figure 36**. Graphic of antioxidant properties in the case of ABTS + VO(oda)(H2O)2

**Table 15**. Data of ABTS + VO(oda)(bpy)

| Absorbance | c[mMol] | S [%] |
|---|---|---|
| 0.47 | 0.16 | 63.07 |
| 0.7 | 0.08 | 41.58 |
| 0.84 | 0.04 | 28.50 |



**Figure 37.** Graphic of antioxidant properties in the case of ABTS + VO(oda)(bpy)
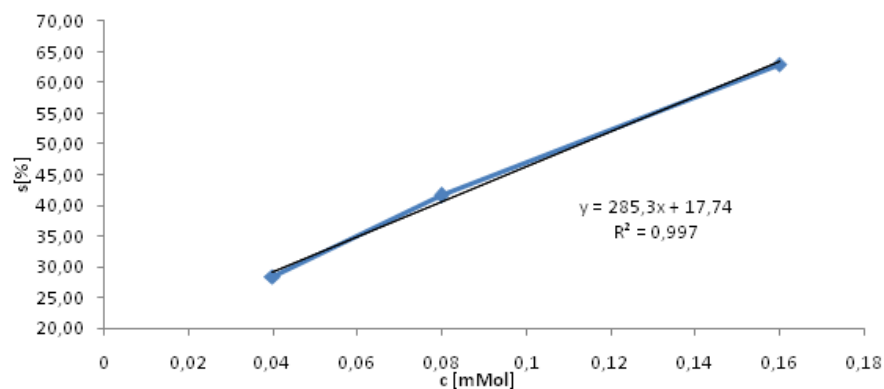
After obtaining equations of each graphic are calculated the $Ic_{50}$ for each case, substituting y for 50 and it is calculate this parameter: $Ic_{50}$=0.083 for ABTS+(oda)(H2O) and $Ic_{50}$= 0.113 for ABTS+(oda)(bpy). Knowing that the ascorbic acid $Ic_{50}$ value is 0.03:

Worse antioxidant than AA<$Ic_{50}$ascorbic acid < Better antioxidant than AA

# 4. CONCLUSIONS

In this paper we have thoroughly investigated the putatice mechanism of action of three oxovanadium (IV) complex with multiple oxygen donor ligands such as oxodiacetate (oda) and related derivates with 2,2-bypyridine and 1,10-phenanthroline.

During this experiment, different compounds have been synthesized, where it can be observed that the yields of each synthesis reaction carried out are acceptable, since yields of between 55 and 86 percent are obtained.

Complexes VO(oda)(bpy) and VO(oda)(phen) may be dissolved in water but are not soluble in solvents of low polarity. They are air stable, both in solution and in the solid state. The effective magnetic moment values of these derivatives are similar to that of VO(oda)(H2O)2 and consistent with one unpaired electron in the ground-state configuration.

To characterize each compound it has been carried out different methods. In the case of the elemental analysis it has proved that the values calculated theoretically are similar than the experimental values, therefore it could say that the obtained compounds have the correct percentages of each elements that takes place in every case

By performing the analysis of the compounds synthesized by the UV-Vis method, the molar absorptivity can be determined, defined as it is a measurement of how strongly a chemical species attenuates light at a given wavelength. It is an intrinsic property of the species. The larger the molar absorptivity, more probable the electronic transition.

In the case of the analysis of antioxidant properties it has been determine, in comparison with ascorbic acid, the quality of the synthesized compounds it is obtained the next conclusion: In view of the results, the compounds have worse antioxidant properties than the ascorbic acid (AA).

VO(oda)(H2O)2 < VO(oda)(bpy)<AA
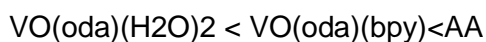
With this experience it has been possible to verify, in a very simple way, the behavior of vanadium compounds, which have multiple applications to diseases that are on the rise today.

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